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A KINETIC STUDY OF THE REACTION OF NITROGEN DIOXIDE WITH TETRAFLUORETHYLENE

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continued on inside back cover

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A Kinetic Study of the Reaction of Nitrogen Dioxide with Tetrafluoroethylene

by

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Abstract

The reaction of NO_2 with C_2F_4 was studied at 30, 68, 114, and 157°C by *in situ* monitoring the infrared absorption bands of the products. The major primary products of the reaction are O_2NCF_2CFO and FNO. Smaller amounts of CF_2O (and presumably NO) are also produced. There was no evidence for other primary products, though they may have been produced in minor amounts.

The rate laws for the production of both O_2NCF_2CFO and CF_2O are first order in both $[NO_2]$ and $[C_2F_4]$. CF_2O production is at least partly heterogeneous as demonstrated by packing the quartz reaction vessel with Pyrex beads and by using a Monel cell. The homogeneous rate constant obtained from the high temperature results gives a rate constant of $3.4 \times 10^8 \exp(-17000/RT)\ \underline{M}^{-1}\text{sec}^{-1}$ for CF_2O production. Actually these Arrhenius parameters represent lower limits, since the heterogeneous reaction may still be playing a significant role. The production rate of O_2NCF_2CFO is not much affected by changing the nature of the surface or the surface to volume ratio. However the reaction may be heterogeneous, since the rate constant for its formation of $1.3 \times 10^4 \exp(-7500/RT)\ \underline{M}^{-1}\ \text{sec}^{-1}$ has an abnormally low preexponential factor.

Experiments in the presence of NO indicate that the mechanism for O_2NCF_2CFO formation is

$$NO_2 + C_2F_3 \rightarrow O_2NCF_2CF_2 \qquad 11$$

$$O_2NCF_2CF_2 + NO_2 \rightarrow O_2NCF_2CFO + FNO \qquad 12$$

The intermediate can also react with NO

$$O_2NCF_2CF_2 + NO \rightarrow O_2NCF_2CF_2NO \qquad 13$$

with $k_{13}/k_{12} = 1.3$.

Introduction

The reactions of NO_2 with perhalogenated olefins have been the subject of several studies dating back to the beginning of this century.[1-6] Kinetic data seem to be rather lacking in this area, however. For this reason, and as part of a continuing investigation of the reactions of atmospheric contaminants, we have undertaken a study of the kinetics of the reaction of NO_2 with C_2F_4.

Coffman et al.[3] and Haszeldine[4] reported that the product of the reaction was 1,2-dinitrotetrafluoroethane. Later, Knunyants and Fokin[5] found that if the reaction were carried out in a solution of $CHCl_3$, $CHClF_2$, CCl_4, or $C_2Cl_2F_4$, the major products were 1,2-dinitrotetrafluoroethane and presumably β-nitrotetrafluoroethylnitrite in about equal amounts. In the gas phase, Fokin et al.[6] reported that the nitrite could be three or four times as important as the dinitro compound.

Later work has indicated that the compound isolated by Fokin et al.[5,6,7] was not the nitrite, but the acetyl fluoride. The identification of the nitrite was based on boiling point, density, and refractive index,[5] but the reported values of these parameters agree almost exactly with those reported later for the acetyl fluoride by the same group.[8] Another argument in the identification of the nitrite was the fact that it underwent hydrolysis,[7] but this has been shown to be true for the acetyl fluoride as well.[9] Furthermore, Andreades[10] could not find the nitrite in a related set of experiments. Finally, Barr and Haszeldine[11] report β-nitrodifluoroacetylfluoride as a known reaction product, and Knunyants et al.[9] found this compound in the reaction of NO_2 with 1,3-C_4F_6.

We have reexamined the gas-phase reaction and have monitored product formation by *in situ* infrared analysis. Our results confirm that the major initial products of the reaction are β-nitrodifluoroacetylfluoride and nitrosylfluoride.

Experimental

Tetrafluoroethylene was obtained from Peninsular ChemResearch Co. and purified by collecting the fraction volatile at -130°C but condensable at -196°C. Nitrogen dioxide was prepared from nitric oxide (Technical Grade - Matheson Co.) and oxygen (Extra Dry Grade - Matheson Co.). The nitric oxide was first purified by collecting the fraction volatile at -160°C in a -196°C trap, degassing, and then reacting with oxygen. The resulting N_2O_4 was degassed at -196°C and stored in a darkened bulb. Only when the condensed solid (N_2O_4) was pure white was it used. Bis(trifluoromethyl)peroxide was obtained from Peninsular ChemResearch Co. and used without further purification.

All pressures were measured on a mercury manometer, a Wallace and Tiernan absolute pressure indicator, or a calibrated alphatron gauge, depending on the gas and the pressure desired. Mixtures were made directly in the reaction vessel. The NO_2 pressure was computed from the total $NO_2 + N_2O_4$ pressure by use of the equilibrium constant for the $N_2O_4 \rightleftarrows 2NO_2$ reaction. The equilibrium constants were obtained from the combined data of several modern investigations,[12-14] and the values used were 0.203 and 1.46 atmospheres at 30 and 68°C respectively. Corrections at 114 and 157°C were not needed as the equilibrium gives essentially NO_2 under all of our conditions.

The reaction took place in a 10-cm long by 5-cm diameter quartz or Pyrex cell with sodium chloride windows. The cell was situated in the sample beam of a Beckman IR-10 infrared spectrometer and was connected by a Teflon stopcock to a conventional high vacuum line. To increase the sensitivity of the infrared analysis, a scale expander was used for some runs at room temperature. For some runs 1000 glass beads of 3 ± 1/2 mm diameter

were added to the quartz cell to determine heterogeneous effects. In this way, the surface area was increased from 220 to 493 cm^2 and the volume was reduced from 200 to 186 cm^3. For several runs a Monel cell with sodium chloride windows was used to permit analysis for FNO. High temperature runs were made with a wire-wound aluminum furnace enclosing the quartz cell. The temperature was measured with a thermocouple placed between the cell and the furnace wall.

During the reaction the 5.12 μ band of CF_2O and the 5.28 μ band of O_2NCF_2CFO could be monitored continually. With the Monel cell the 5.42 μ band of FNO was also monitored. The absorption coefficient of nitrosyl fluoride was determined by reacting NO and CF_3OOCF_3 in the Monel cell and monitoring the production of FNO and CF_2O. These two products have been reported[15] to be produced in equal amounts. For the 5.12 μ band of CF_2O the extinction coefficient (to base 10) is 0.011 $torr^{-1}cm^{-1}$ at room temperature.[16] Thus for FNO we found the extinction coefficient (to base 10) to be .0037 $torr^{-1}cm^{-1}$ at room temperature. This value agrees satisfactorily with the approximate value of 0.0024 derived from the infrared spectrum of FNO obtained on a different instrument.[17] The absorption coefficient (to base 10) used for O_2NCF_2CFO was .0088 $torr^{-1}cm^{-1}$ at room temperature and was obtained by equating the rates of FNO and O_2NCF_2CFO production in the Monel cell. It was assumed that the molar extinction coefficients were the same at all temperatures. Actually a slight drop at elevated temperatures might be expected due to temperature broadening. However, earlier work[16] showed no temperature dependence for CF_3CFO between 25 and 125°C and only a minor change for CF_2O over the same temperature range. Any minor effect would be lost in our experimental uncertainty and was therefore ignored.

Attempts to isolate the products after a run met with failure. Both vacuum distillation and gas chromatographic separation were tried. In one series of runs the loss of C_2F_4 was measured by gas chromatography utilizing thermistor detectors and a 10-ft long Porapak Q column at 0°C with a He flow rate of 60 cc/min.

A mass spectrum of a mixture reacted to completion showed major peaks above m/e 28 at m/e 30 (NO^+), 31 (CF^+), 46 (NO_2^+), and 69 (CF_3^+). None of these peaks are useful for diagnostic purposes since any set of products would show them. The CF_3^+ ion is a common rearrangement ion for all fluorocarbons, even if they do not contain CF_3 groups, and it has been observed in the mass spectra of perfluoroacylfluorides.[10] The next two largest mass spectral peaks were at m/e 47 (CFO^+) and 97 (CF_2CFO^+). These peaks are diagnostic for acid fluorides. The peak at m/e 96 ($O_2NCF_2^+$) which would be expected to be important in the dinitro or nitro nitrite compound had an intensity only 2% of that for the 97 peak, and could also be produced from the nitro acetyl fluoride.

Results

In the quartz cell the products of the reaction directly identified by *in situ* infrared analysis were CF_2O and SiF_4. A very strong band at 5.28 μ was seen, which must be the carbonyl stretching band of a -CFO group. We have associated it with the O_2NCF_2CFO molecule, since this molecule has been reported to be a product of the reaction, and has a band at 5.28 μ.[10] Also seen were bands at about 6 μ which can be associated with nitro, nitrite, and nitroso compounds, all of which have been reported as products of the reaction,[3-6,11,18,19] Presumably NO was also produced though no attempts were made to isolate it because of its rapid reaction with NO_2 when condensed. It was not possible to ascertain the presence or absence of tetrafluoroethylene oxide because its characteristic band at 6.22 μ was obscured by NO_2, and it is too unstable to isolate small amounts. The bands of $(FCO)_2$ were absent. In the Monel cell, SiF_4 was not formed but FNO was.

The initial rates of CF_2O and O_2NCF_2CFO production for the various experiments are given in Table I. All indicated pressures are at the temperature of the experiments. The NO_2 pressure was computed from the sum of NO_2 and N_2O_4 pressures by use of the equilibrium constants as indicated in the Table. At any temperature the rates of product formation increase with the product of reactant pressures. If second order kinetics are valid then the following rate laws should be obeyed.

$$R\{O_2NCF_2CFO\} = k[NO_2][C_2F_4] \qquad 1$$

$$R\{CF_2O\} = k'[NO_2][C_2F_4] \qquad 2$$

where R{x} is the rate of production of x.

Figures 1 and 2 show plots based on Equations 1 and 2, respectively. Though there is considerable scatter in the data, the log-log plots can

be fitted by straight lines of slope one. The intercepts give the rate constants k and k' which are listed in Table II. These constants increase with temperature. At 30°C, k is the same for the unpacked and packed quartz cell and the Pyrex cell, but it is slightly reduced in the Monel cell. This reduction is barely outside the experimental uncertainty. Our results seem to indicate that heterogeneous effects are unimportant for O_2NCF_2CFO production. On the other hand, k' is different in the three cells at room temperature. The rate constant in the quartz cell is greater than that in the Monel cell. Packing the quartz cell further raises the rate constant. Thus CF_2O formation must be at least partly heterogeneous.

The Arrhenius plots for the rate constants are shown in Figure 3. The values for k lie on a straight line as expected for a homogeneous reaction. The Arrhenius expression gives $k = 1.3 \times 10^4 \exp(-7500/RT)$ $\underline{M}^{-1}sec^{-1}$ where the activation energy is in calories per mole. The Arrhenius plot for k' is not linear thus indicating two paths for formation of CF_2O. Presumably these are a heterogeneous and homogeneous path, with the latter dominating at high temperatures. If the two high temperature points are fitted to the Arrhenius form, an activation energy of 17.0 kcal/mole and a reasonable preexponential factor of 3.4×10^8 $\underline{M}^{-1}$ sec^{-1} are obtained.

It is desirable to know the stoichiometry of the reaction, i.e. what percentage of the reactants consumed become O_2NCF_2CFO and CF_2O. Ideally this could be determined by monitoring reactant removal during a run. Unfortunately such experiments cannot be done by infrared spectroscopy since the products have absorption bands which overlap all the useful reactant absorption bands. Furthermore if C_2F_4 is in excess, so that

the NO_2 is consumed, then NO is produced which interferes with the reaction by competing with NO_2 for the reaction intermediates. However with NO_2 in large excess, so that the NO accumulation is relatively unimportant compared to NO_2, then C_2F_4 removal measurements should be meaningful if the difficulty of product interference in the analysis could be overcome. We attempted this by two ways in two different series of experiments.

In one series of experiments the rate of C_2F_4 consumption was determined by measuring the amount of C_2F_4 remaining after various reaction times. Several experiments were made with the same initial concentrations of NO_2 and C_2F_4, the NO_2 being in large excess. The experiments were conducted for different reaction times; the reacted gases then were expanded into a cold trap at -196°C. The trap was next warmed to -130°C; the C_2F_4 was then vaporized and collected in another trap at -196°C for gas chromatographic analysis.

Figure 4 shows a plot of the remaining C_2F_4 pressure as a function of reaction time. The initial rate of C_2F_4 removal was 0.064 Torr min^{-1}, which corresponds to a rate constant of about 3.8×10^{-6} $Torr^{-1}sec^{-1}$ at 33°C for the initial NO_2 and C_2F_4 pressures of 63 Torr and 4.41 Torr, respectively. The sum of the rate constant for formation of O_2NCF_2CFO plus one-half that for CF_2O formation is about 2.9×10^{-6} $Torr^{-1}sec^{-1}$ under the same conditions. Thus about 75% of the C_2F_4 consumption can be accounted for by O_2NCF_2CFO and CF_2O.

The problem with the above series of experiments is that it is difficult to quench the reaction at a given time and be certain that all reaction ceases. Though the temperature is drastically reduced, the gases also condense, and some liquid-phase reaction might proceed. There is some evidence for this from Figure 4. As the reaction time is enhanced,

the rate of C_2F_4 consumption should drop because the reactants are being consumed. However no drop is evident in Figure 4 even though for the last point, about 75% of the C_2F_4 has been consumed. Thus some reaction after quenching (or a change in the gas-phase reaction mechanism with conversion) is indicated. Consequently the 75% conversion to acid fluoride products should be considered a lower limit. To circumvent this difficulty another method was employed to attempt to ascertain the stoichiometry.

The rate of C_2F_4 consumption can also be deduced from the rate of CF_2O production if the rate law remains unchanged as the reaction proceeds to completion. This should be the case in the presence of a large excess of NO_2, so that the NO produced does not effectively compete with the NO_2 as a reactant. Furthermore under these conditions the NO_2 pressure remains nearly constant during the reaction. The integrated rate law can then be written in the form

$$[CF_2O] = \alpha[C_2F_4]_0\{1-\exp(-k'[NO_2]_{av}t/\alpha\} \qquad 3$$

where t is the reaction time, $[NO_2]_{av}$ is the average value of $[NO_2]$ during the run, and α is the ratio of CF_2O produced to C_2F_4 consumed. Equation 3 can be fitted to the data by an iterative process. Values of α are guessed and the exponential term is computed and plotted against $[CF_2O]$. The resulting plot should be linear, pass through the origin, and have a slope of $\alpha[C_2F_4]_0$. Various values of α are assumed until the best fit is obtained.

Figure 5 shows plots of $[CF_2O]$ vs. $1-\exp(-k'[NO_2]_{av}t/\alpha)$ for one run in the unpacked quartz vessel at each temperature. Reasonable plots are obtained which satisfy all the required criteria. Values of α obtained from the plots are listed in Table II.

In principle a similar set of plots for O_2NCF_2CFO should be possible. Actually, however, the infrared absorption due to O_2NCF_2CFO becomes total

early in the reaction, and this product cannot be monitored in the later stages of the reaction.

The fraction of C_2F_4 which becomes O_2NCF_2CFO plus CF_2O can be computed directly as $\alpha(2k + k')/2k'$. This fraction is listed in Table II at each temperature. The fraction computed in this way exceeds one at three of the temperatures. Of course, in actuality, the fraction cannot exceed one. Our computation has considerable error because of the experimental uncertainties in both k' and α. Furthermore, the extinction coefficient for O_2NCF_2CFO is not well known.

In spite of the uncertainty, it is clear that O_2NCF_2CFO is the major initial product of the reaction. We found no evidence for either $O_2NCF_2CF_2NO_2$ or $O_2NCF_2CF_2ONO$. If the dinitro or nitro-nitrite compounds are produced at all, they must be minor products.

Discussion

The overall stoichiometries for the various processes are:

$$C_2F_4 + 2NO_2 \rightarrow O_2NCF_2CFO + FNO \quad (4)$$

$$\rightarrow 2CF_2O + 2NO \quad (5)$$

$$\rightarrow O_2NCF_2CF_2NO_2 \quad (6)$$

$$\rightarrow O_2NCF_2CF_2ONO \quad (7)$$

$$C_2F_4 + NO_2 \rightarrow \overline{OCF_2CF_2} + NO \quad (8)$$

No one has reported $\overline{OCF_2CF_2}$ as a product, though no one has had a suitable analytical method. In any event it, as well as $O_2NCF_2CF_2NO_2$ and $O_2NCF_2CF_2ONO$, must be minor products if they are produced at all. The FNO produced was not seen in the quartz or Pyrex vessels due to the rapid reaction between FNO and SiO_2 to produce SiF_4, which was seen.

The detailed scheme for the reaction must involve at least two steps:

$$NO_2 + C_2F_4 \rightleftharpoons I \quad (9)$$

$$I + NO_2 \rightarrow \text{Products} \quad (10)$$

where I is one or more intermediates. For the production of O_2NCF_2CFO and CF_2O, the rate of the reverse of Reaction 9 must be slow compared to the rate of Reaction 10 in order to explain the first-order dependence of the rate law on $[NO_2]$.

For CF_2O production, a number of intermediates can be envisioned. For example the reaction might proceed via

$$NO_2 + C_2F_4 \rightarrow ONOCF_2CF_2$$

$$ONOCF_2CF_2 + NO_2 \rightarrow ONOCF_2CF_2ONO \rightarrow 2NO + 2CF_2O$$

or

$$NO_2 + C_2F_4 \rightarrow NO + \overline{OCF_2CF_2}$$

$$\overline{OCF_2CF_2} + NO_2 \rightarrow NO + 2CF_2O$$

or

$$NO_2 + C_2F_4 \rightarrow NO + CF_2O + CF_2$$

$$CF_2 + NO_2 \rightarrow CF_2O + NO$$

All of the above schemes give the proper stoichiometry, lead to the observed rate law, and predict a normal Arrhenius preexponential factor (i.e. $\sim 10^8 \underline{M}^{-1}sec^{-1}$) as observed for the high temperature (presumably homogeneous) results. Since the reaction is partly heterogeneous, one of the above schemes may dominate in the gas phase and another on the wall.

For O_2NCF_2CFO production two schemes can be envisioned:

$$NO_2 + C_2F_4 \rightarrow O_2NCF_2CF_2 \qquad 11$$

$$O_2NCF_2CF_2 + NO_2 \rightarrow O_2NCF_2CFO + FNO \qquad 12$$

or

$$NO_2 + C_2F_4 \rightarrow FNO + CF_2CFO$$

$$NO_2 + CF_2CFO \rightarrow O_2NCF_2CFO$$

In the former case the intermediate is $O_2NCF_2CF_2$. There is no doubt that this intermediate exists, since if NO is also present, $O_2NCF_2CF_2NO$ is produced in abundance[18,19]

$$O_2NCF_2CF_2 + NO \rightarrow O_2NCF_2CF_2NO \qquad 13$$

However it is possible that the $O_2NCF_2CF_2$ intermediate is not the precursor for the acid fluoride.

In order to differentiate between these two schemes, several experiments were run with added NO. The first mechanism above predicts a strong suppression of the acetyl fluoride in the presence of NO. In the second scheme, the intermediate may add to NO as well as NO_2, but in either case an acid fluoride will be produced. Since all acid fluorides have strong absorptions at 5.25-5.30μ, the infrared absorption at those wavelengths should not be markedly affected.

The results of the experiments with added NO are shown in Table III. It is clear that as $[NO]/[NO_2]$ is increased, acid fluoride production is markedly reduced. Therefore we conclude that the mechanism for acid fluoride production consists of Reactions 11-13. This mechanism predicts that

$$\frac{[NO_2][C_2F_4]}{R\{O_2NCF_2CFO\}} = k_{11}^{-1}(1 + k_{13}[NO]/k_{12}[NO_2]) \quad 14$$

In the absence of NO, the expression is just a rearrangement of Equation 1, so that the empirical rate constant k can be associated with Reaction 11.

Figure 6 is a plot based on Equation 14. The left-hand side of the equation is plotted vs $[NO]/[NO_2]$ and a reasonable straight line results with a slope of 0.48×10^6 Torr sec and an intercept of 0.36×10^6 Torr sec. The ratio of slope to intercept gives $k_{13}/k_{12} = 1.3$.

The low value of 1.3×10^4 $\underline{M}^{-1}sec^{-1}$ found for the Arrhenius pre-exponential factor for k is most difficult to understand. The rate coefficient is that associated with Reaction 11, and it should have a pre-exponential factor at least 1000 times larger. One possibility is that the reaction is not homogeneous, but occurs on the surface. In fact the rate constant in the Monel cell is only about 70% of that in the quartz cell. However the difference is not outside the experimental uncertainty. Furthermore the rate constants are the same in the packed and unpacked quartz cell and in the Pyrex cell. Finally there is no deviation from linearity in the Arrhenius plot, as would be expected if both homogeneous and heterogeneous processes were occurring. Nevertheless Reaction 11 is probably heterogeneous, in spite of the fact that the rate constant is not much affected by changing the nature of the surface or the surface to volume ratio.

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Table 1

Rates of Product Formation in the Reaction of NO_2 with C_2F_4

$[C_2F_4]$, Torr	$[NO_2]+[N_2O_4]$, Torr	$[NO_2]$, Torr[a]	$10^{-3}[NO_2][C_2F_4]$, $Torr^2$	$R\{O_2NCF_2CFO\}$, μ/sec	$R\{CF_2O\}$, μ/sec
		T = 30 ± 1°C, Quartz Cell			
13	79	58	0.75	2.07	0.08
30	29.7	25.5	0.76	-	0.091[b]
54	16.8	15.3	0.83	-	0.084[b]
39	28	24	0.94	2.90	0.09
18	90	64	1.14	3.71	0.12
117	13	12	1.40	3.54	0.17
22	88	63	1.41	-	0.165[b]
111	15.0	13.8	1.53	3.50	-
46	47.6	38.2	1.76	-	0.217[b]
36	90	64	2.28	6.94	0.33
66	45.0	36.4	2.40	-	0.326[b]
47	88	63	2.96	9.04	-
35	167	102	3.57	11.75	-
235	40	33	7.76	26.90	-
216	53	41	8.95	-	0.79[b]
230	60	46	10.7	-	0.98[b]
		T = 68 ± 1°C, Quartz Cell			
14.4	25.4	24.8	0.358	2.77	0.21
11.3	65	61.5	0.695	5.72	0.45
64	23	22.5	1.440	13.30	0.62
28	67	63.5	1.780	13.70	0.85
		T = 114 ± 1°C, Quartz Cell			
14.2	9.0	9.0	0.128	2.91	0.63
6.3	37.8	37.8	0.238	7.00	0.97
24.1	11.2	11.2	0.270	5.80	1.07
35.7	9.4	9.4	0.336	10.20	1.09

Table 1

(Continued)

$[C_2F_4]$, Torr	$[NO_2]+[N_2O_4]$, Torr	$[NO_2]$, Torr[a]	$10^{-3}[NO_2][C_2F_4]$, Torr^2	$R\{O_2NCF_2CFO\}$, μ/sec	$R\{CF_2O\}$, μ/sec
		T = 157 ± 1°C, Quartz Cell			
12.3	6.0	6.0	0.074	3.87	2.03
8.6	17.2	17.2	0.148	11.89	4.76
8.3	33.1	33.1	0.275	22.95	10.85
12.4	24.5	24.5	0.304	24.42	10.60
		T = 30 ± 1°C, Monel Cell			
16.5	82	60	0.980	1.97	0.06
154	6.6	6.3	0.985	1.82	-
54	31	26.5	1.43	2.66	0.07
28	114	76	2.14	4.06	0.15
195	12	11.2	2.19	4.13	-
170	38	31.5	5.35	13.10	0.26
		T = 30 ± 1°C, Packed Quartz Cell			
14.2	52	40	0.573	1.35	0.11
134	21.3	19.0	2.54	6.77	-
31.4	140	89	2.79	7.35	0.66
		T = 33 ± 1°C, Pyrex Cell			
133	21.0	18.7	2.49	7.45	-
4.41	86	62	0.27	0.68	-
4.41	88	64	0.28	0.76	-
4.41	87	63	0.28	0.68	-
4.41	87	63	0.28	0.78	-
4.41	88	64	0.28	0.77	-
4.41	88	64	0.28	0.69	-
4.41	87	63	0.28	0.76	-

a) Computed from K_p for $N_2O_4 = 2NO_2$. K_p = 0.203 and 1.46 atm, respectively, at 30 and 68°C.[12-14]

b) Scale expander employed.

Table II

Rate Constants

Temp, °C	Cell	10^6 k, $Torr^{-1}sec^{-1}$	k, $\underline{M}^{-1}sec^{-1}$	10^6 k', $Torr^{-1}sec^{-1}$	k', $\underline{M}^{-1}sec$	α	$\frac{\alpha(2k + k')}{2k'}$
33	Pyrex	2.8	0.053	-	-	-	-
30	Monel	2.0	0.038	0.058	0.00110	-	-
30	Packed	2.6	0.049	0.230	0.00435	-	-
30	Quartz	2.8	0.053	0.114	0.00216	0.060	1.4
68	"	8.2	0.182	0.58	0.0123	0.080	1.2
114	"	26	0.62	3.9	0.094	0.17	1.2
157	"	68	1.83	31	0.83	0.32	0.9

$k = 1.3 \times 10^4 \exp(-7500/RT)\ \underline{M}^{-1}sec^{-1}$

$k' = 3.4 \times 10^8 \exp(-17000/RT)\ \underline{M}^{-1}sec^{-1}$ (Based on results at 114 and 157°C only)

Table III

Rates of Acid Fluoride Formation in the Reaction of NO_2 with C_2F_4 in the Presence of NO at 33°C in the Pyrex Cell

$\frac{[NO]}{[NO_2]}$	[NO], Torr	$[NO_2]+[N_2O_4]$, Torr	$[NO_2]$, Torr[a]	$[C_2F_4]$, Torr	$R\{O_2NCF_2CFO\}$, μ/sec
0.0	0.0	21.0	18.7	133	7.4
0.0	0.0	21.3	19.0	151	8.1
3.44	67	22.0	19.5	155	2.2
11.2	139	13.4	12.4	67	0.14
11.3	224	22.4	19.8	154	0.5

a) Computed from K_p for $N_2O_4 = 2NO_2$.[12-14]

List of Figures

Fig. 1: Log-log plots of R{O_2NCF_2CFO} vs. $[NO_2][C_2F_4]$ in the reaction of NO_2 with C_2F_4.

Fig. 2: Log-log plots of R{CF_2O} vs. $[NO_2][C_2F_4]$ in the reaction of NO_2 with C_2F_4.

Fig. 3: Arrhenius plot of k and k', the respective reaction rate constants for O_2NCF_2CFO and CF_2O production, vs. reciprocal temperature.

Fig. 4: Plot of C_2F_4 pressure vs. reaction time in the reaction of C_2F_4 with NO_2 at 33°C for initial pressures of 4.41 and 63 torr, respectively, for C_2F_4 and NO_2.

Fig. 5: Plot of CF_2O pressure vs. $1-\exp(-k'[NO_2]_{av}t/\alpha)$ in the reaction of NO_2 with C_2F_4 for four experiments in the unpacked quartz cell. Reaction conditions for the four runs are:

Temp. °C	$[C_2F_4]_0$, Torr	$[NO_2]_{av}$, Torr	k', $Torr^{-1}sec^{-1}$	α
157	8.3	33.0	3.9×10^{-5}	0.32
114	1.8	40.0	6.4×10^{-6}	0.17
68	4.4	35.0	7.2×10^{-7}	0.08
30	35	80	1.5×10^{-7}	0.06

Fig. 6: Plot of $[NO_2][C_2F_4]/R\{O_2NCF_2CFO\}$ vs $[NO]/[NO_2]$ in the reaction of NO_2 with C_2F_4 in the presence of NO at 33°C.

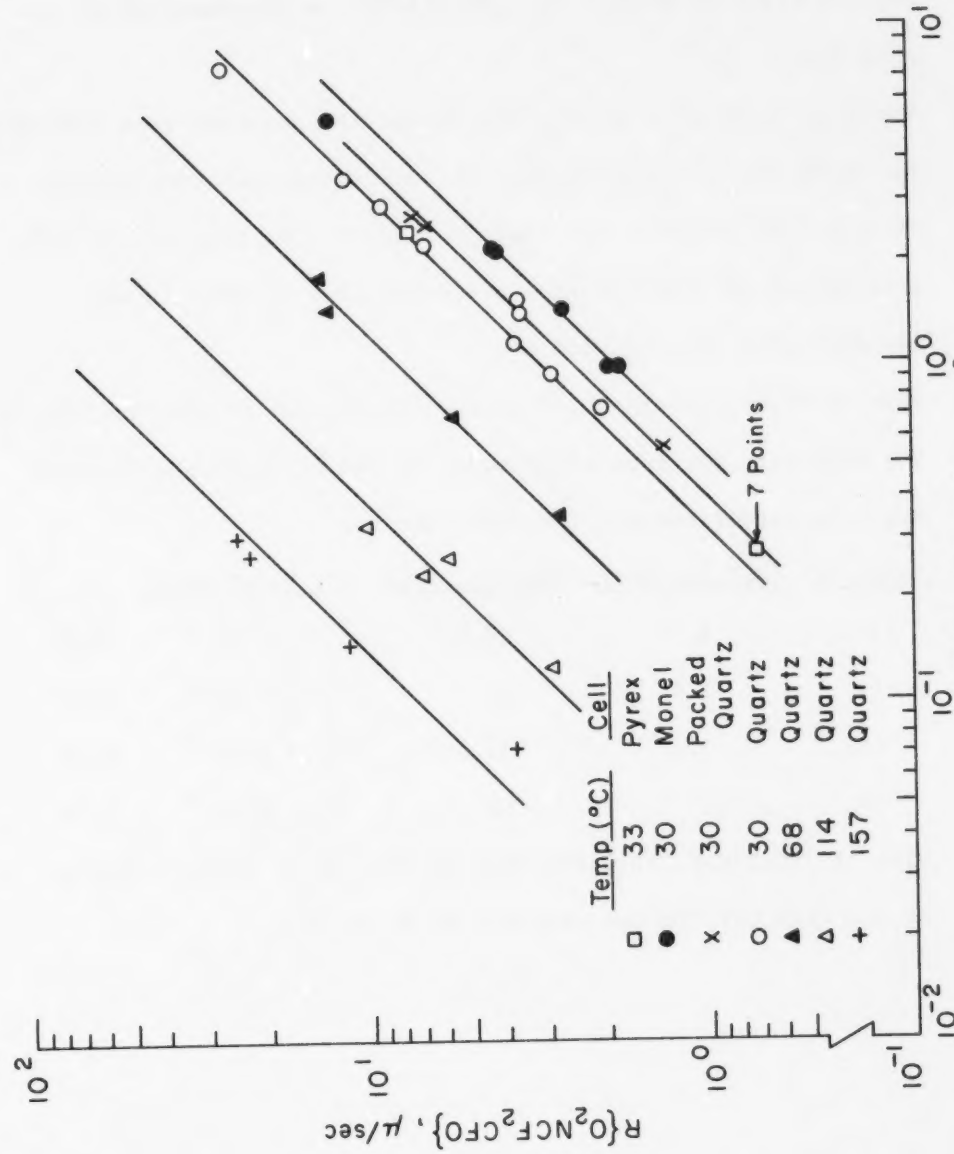
R{O2NCF2CFO}, μ/sec
10^2
10^1
10^0
10^-1
10^-2
10^-1
10^0
10^1
10^-3[NO2][C2F4], Torr^2
Temp (°C)
Cell
□ 33 Pyrex
● 30 Monel
× 30 Packed Quartz
○ 30 Quartz
▲ 68 Quartz
△ 114 Quartz
+ 157 Quartz
7 Points

Figure 1

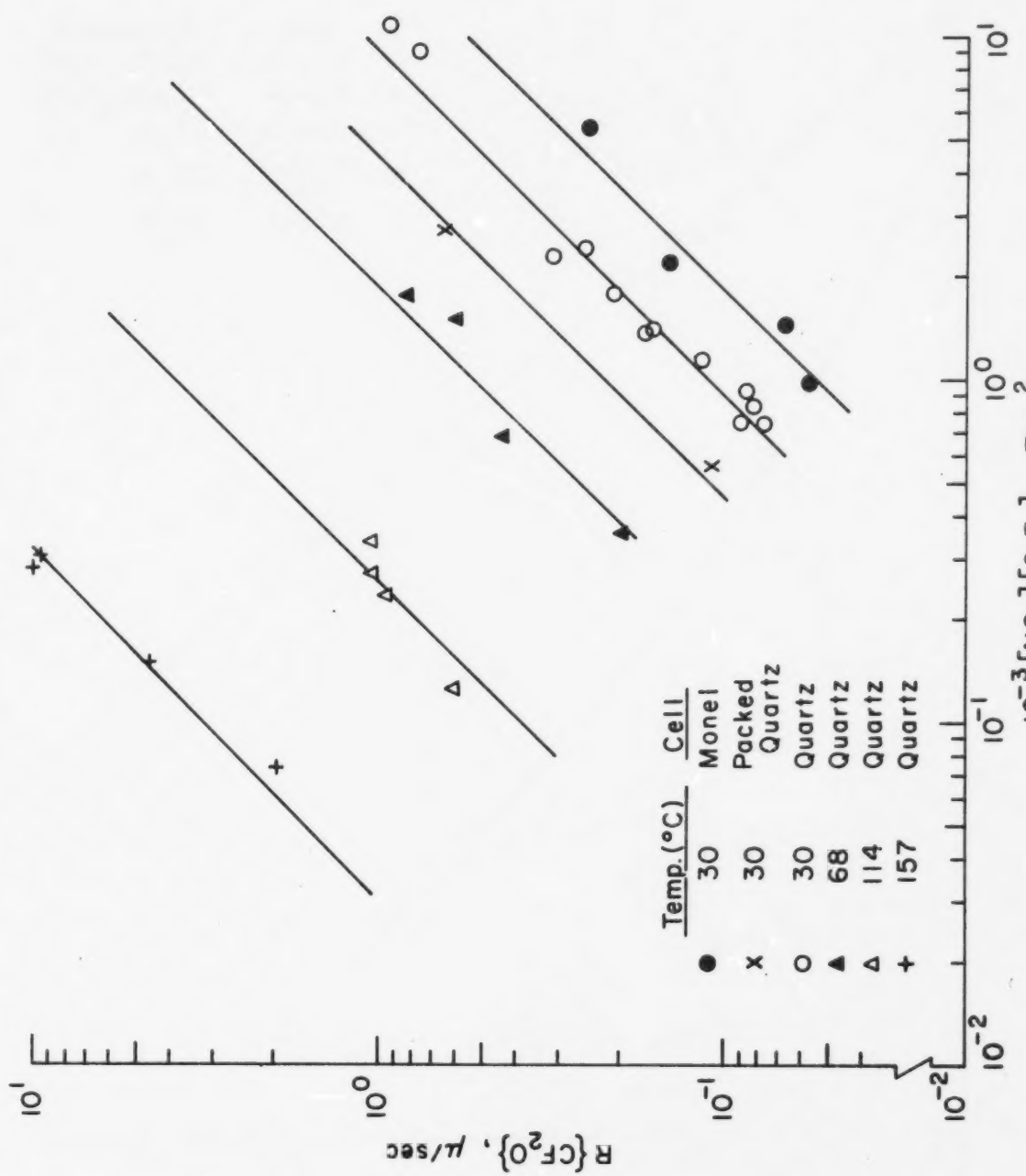
R{CF2O}, μ/sec
10^1
10^0
10^-1
10^-2
10^-2
10^-1
10^0
10^1
10^-3 [NO2][C2F4], Torr^2
Temp.(°C) Cell
● 30 Monel
x 30 Packed Quartz
○ 30 Quartz
▲ 68 Quartz
△ 114 Quartz
+ 157 Quartz

Figure 2

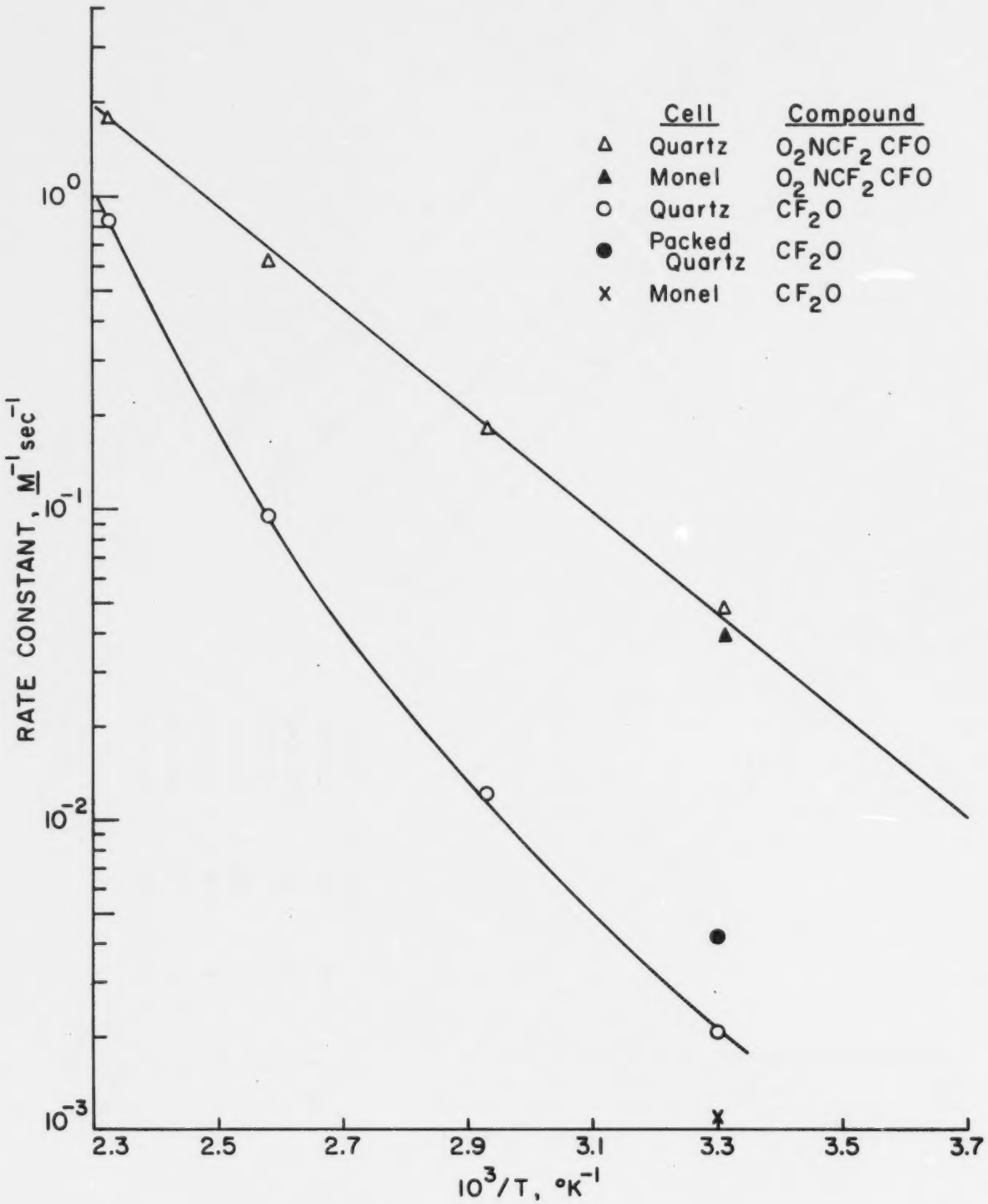
Cell
Compound
Quartz
O_2NCF_2CFO
Monel
O_2NCF_2CFO
Quartz
CF_2O
Packed Quartz
CF_2O
Monel
CF_2O
RATE CONSTANT, $M^{-1}sec^{-1}$
10^0
10^{-1}
10^{-2}
10^{-3}
2.3
2.5
2.7
2.9
3.1
3.3
3.5
3.7
$10^3/T$, $°K^{-1}$

Figure 3

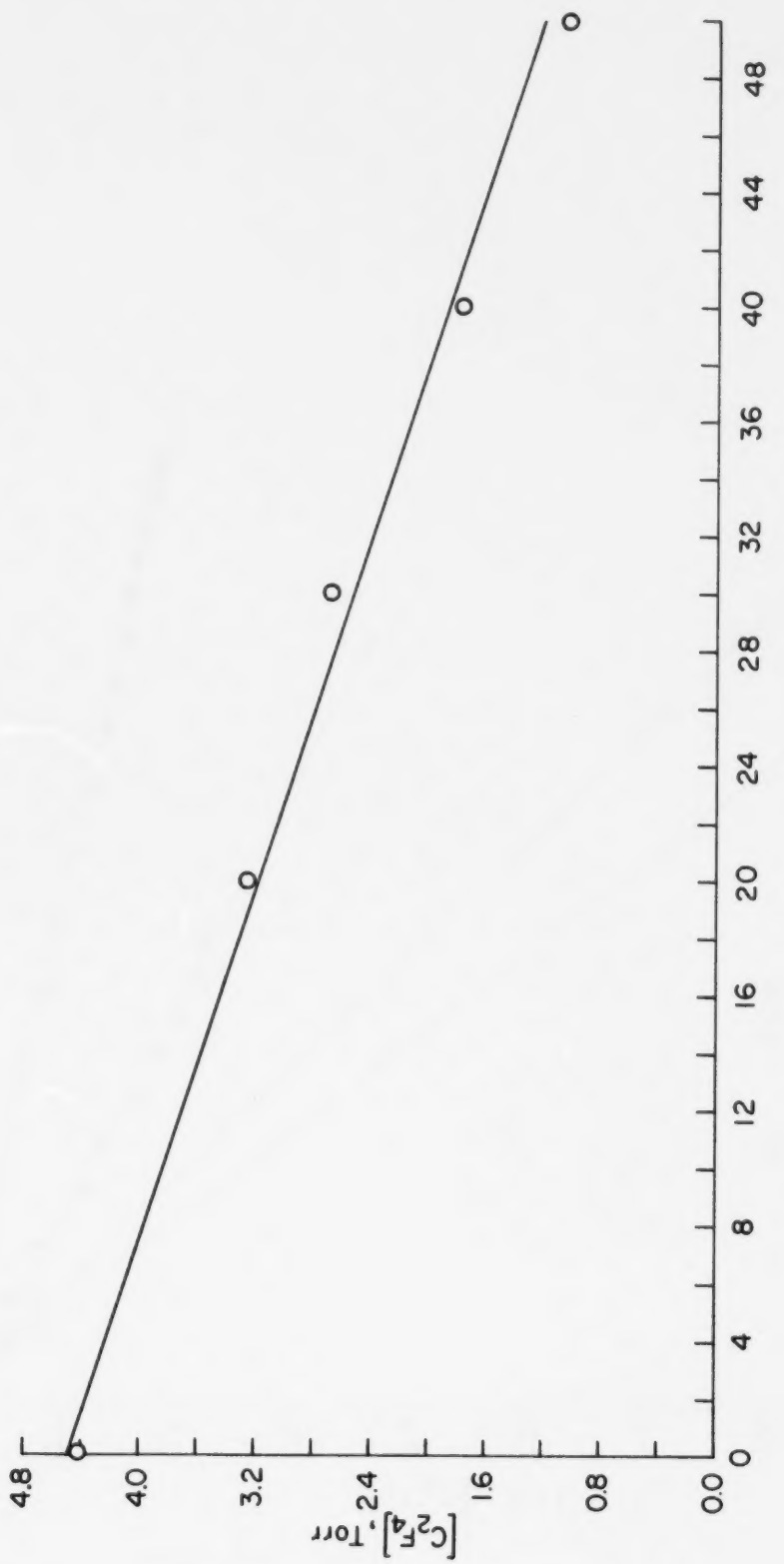
4.8
4.0
3.2
2.4
1.6
0.8
0.0
[C2F4], Torr
0
4
8
12
16
20
24
28
32
36
40
44
48
TIME, MIN.

Figure 4

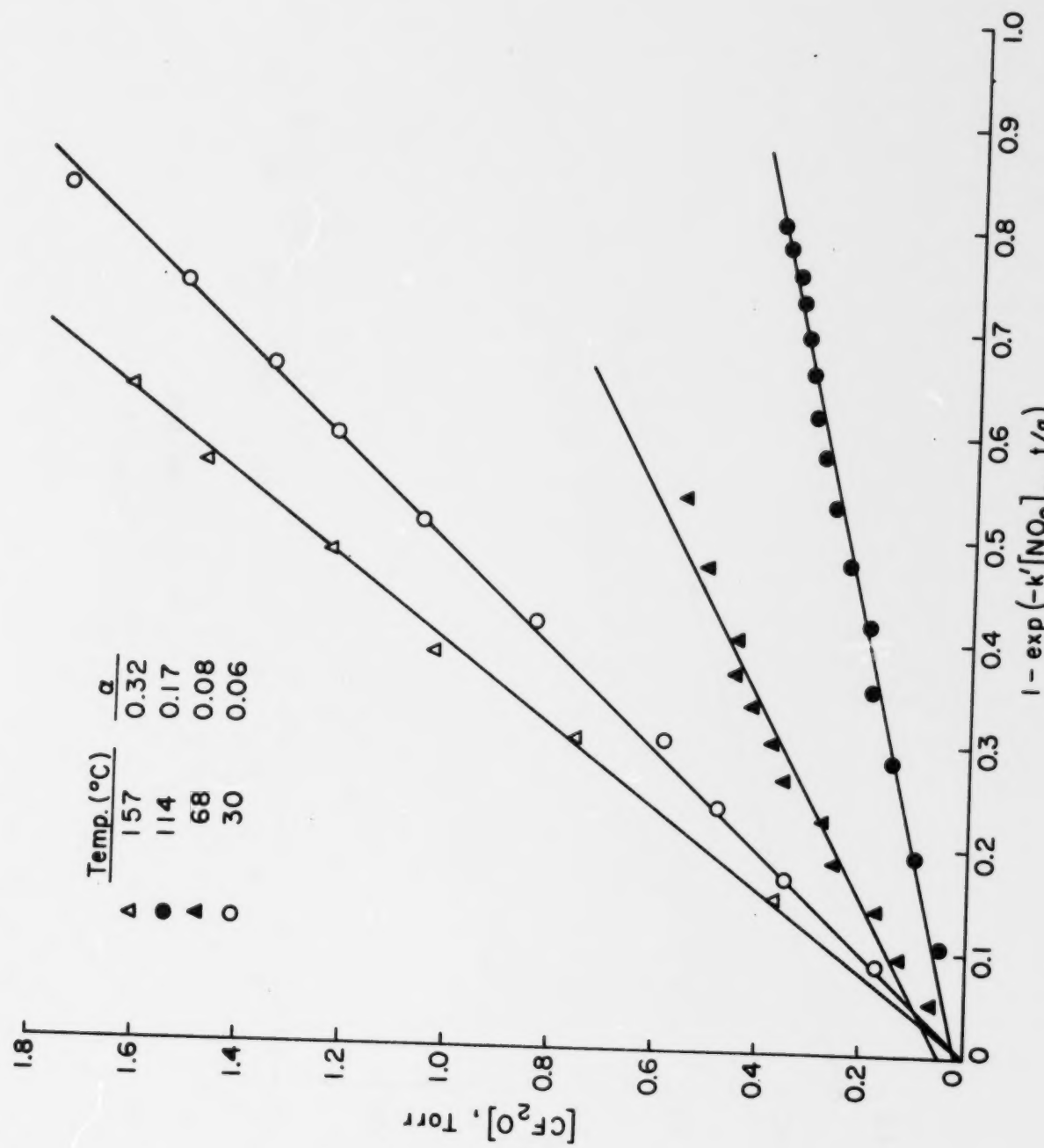

Figure 5

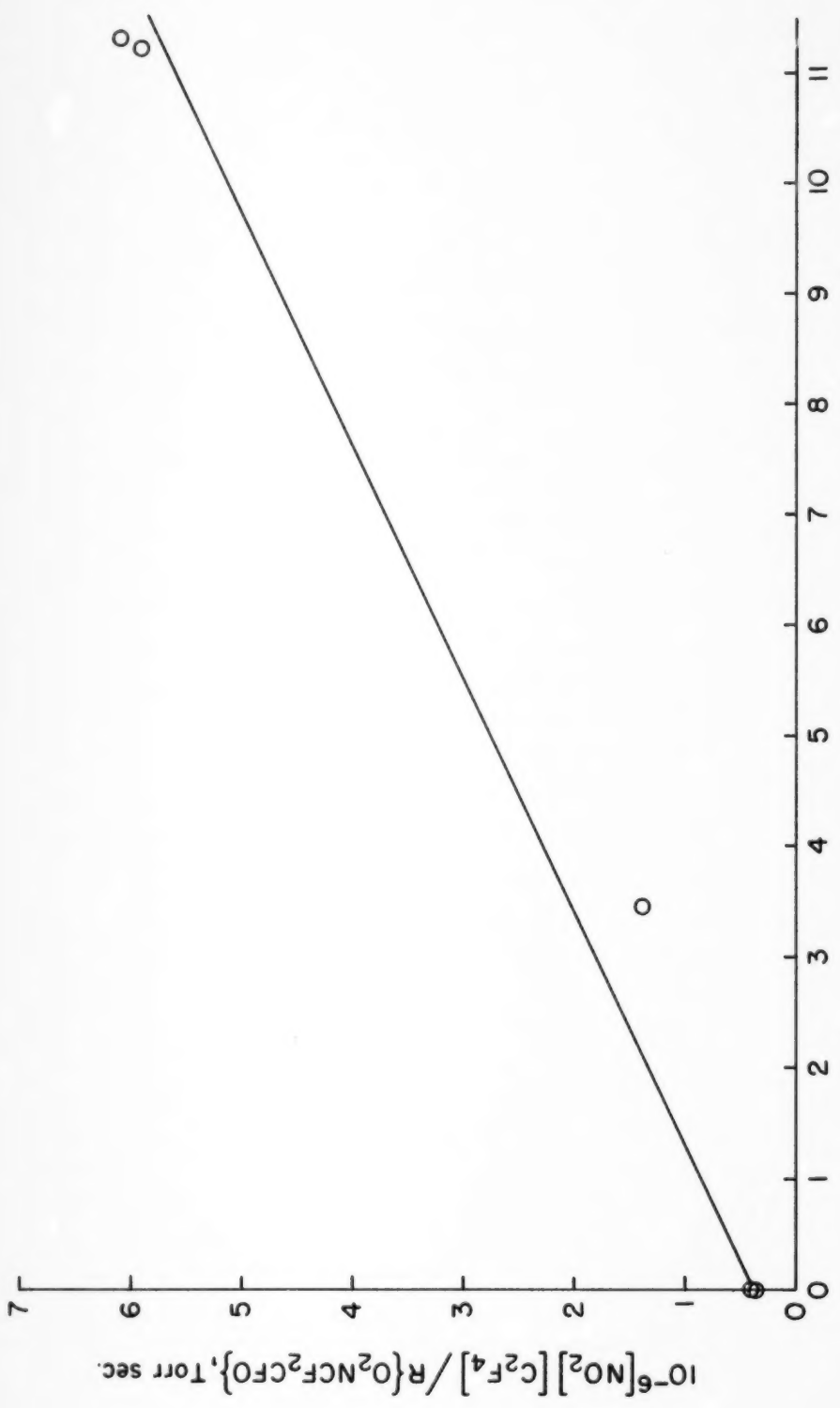

Figure 6

The Air Pollution Analysis Instrumentation course is designed for the associate degree student and air pollution control agency technicians to provide specialized training in the operation, maintenance and data analysis of air pollution control instrumentation. Both courses are offered during the summer at the University Park Campus.

A two year course leading to the Associate Degree in Air Pollution Technology is given at the Berks Campus of The Pennsylvania State University. The graduate of this program is trained to be responsible for the calibration, installation, and operation of air sampling and monitoring equipment. He may also be expected to investigate complaints, conduct plant inspections, make source evaluations, and formulate recommendations based on his findings.

Address requests for more information concerning the training programs to the Director, Center for Air Environment Studies, 226 Chemical Engineering II, The Pennsylvania State University, University Park, Pennsylvania 16802.

Publications Available

AIR POLLUTION TITLES, a current awareness publication service, is available on a January-December subscription basis. This publication is a quick guide to current literature and has some capacity as a retrospective searching tool. APT uses a computer-produced, Keyword-in-Context (KWIC) format to provide a survey of current air pollution and related literature. During the year over 1,000 journals are scanned for pertinent citations.

Subscriptions to APT at $15/year, cover issues per year as follows: No. 1, January-February; No. 2, March-April; No. 3, May-June; No. 4, July-August; No.5, September-October; No. 6, cumulative issue for the year, including November-December citations. The 1972 subscription of APT is now available. Cumulative issues for 1967, 1968, 1969, 1970, and 1971 are available; the cost is $10 each.

INDEX TO AIR POLLUTION RESEARCH was published in July of 1966, 1967, and 1968. Each Index included government sponsored research in the air pollution field and the results of a survey of air pollution research projects conducted by the industrial, sustaining, and corporate members of the Air Pollution Control Association and the American Industrial Hygiene Association, and research supported by other industries and non-profit organizations.

The Index utilizes the Keyword-in-Context (KWIC) format for rapid scanning of project titles. In addition, this publication provides a complete bibliography including mailing addresses where additional information about the project may be obtained. Beginning with the 1967 edition, a section containing citations of papers resulting from the research in progress was included. Copies of the 1966 edition are available at $1.25; the 1968 edition costs $2.

A GUIDE TO AIR POLLUTION RESEARCH: 1969 (PHS Pub. No. 981) was prepared by the Center for Air Environment Studies under contract to the National Air Pollution Control Administration of the U.S.P.H.S. It is available from Superintendent of Documents at a cost of $1.50. The 1971 edition of the Guide is being prepared by the Center under contract to the Office of Air Programs of the Environmental Protection Agency; it will be available from the Superintendent of Documents in late 1972.

HANDBOOK OF EFFECTS ASSESSMENT VEGETATION DAMAGE was published in 1969 as part of the survey of vegetation damage. It describes in detail the many sources of pollution and the effect of pollutants on vegetation; color pictures showing characteristics of plant damage symptoms are included. The cost is $6.

Requests for additional information and orders should be addressed to: Information Services, Center for Air Environment Studies, 226 Chemical Engineering II, University Park, Pennsylvania 16802.